



(11)

EP 2 032 730 B1

(12)

## EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:  
**11.08.2010 Bulletin 2010/32**

(51) Int Cl.:  
**C22C 28/00 (2006.01)** **G21C 3/17 (2006.01)**  
**C01B 3/00 (2006.01)**

(21) Application number: **07790105.6**

(86) International application number:  
**PCT/IT2007/000373**

(22) Date of filing: **29.05.2007**

(87) International publication number:  
**WO 2007/148362 (27.12.2007 Gazette 2007/52)**

(54) **NON-EVAPORABLE GETTER ALLOYS BASED ON YTTRIUM FOR HYDROGEN SORPTION**

NICHT VERDAMPFBARE GETTERLEGIERUNGEN AUF YTTRIUM-BASIS ZUR SORPTION VON WASSERSTOFF

ALLIAGES DE GETTER NON ÉVAPORABLES PARTICULIÈREMENT APPROPRIÉS POUR LA SORPTION D'HYDROGÈNE

(84) Designated Contracting States:  
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR  
HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE  
SI SK TR**

(30) Priority: **19.06.2006 IT MI20061173**

(43) Date of publication of application:  
**11.03.2009 Bulletin 2009/11**

(73) Proprietor: **SAES GETTERS S.p.A.  
20020 Lainate (Milano) (IT)**

(72) Inventors:

- CODA, Alberto  
I-21040 Gerenzano VA (IT)
- CORAZZA, Alessio  
I-22030 Como - Camnago Volta CO (IT)
- GALLITOGNOTTA, Alessandro  
I-21040 Origgio VA (IT)
- TOIA, Luca  
I-210040 Carnago VA (IT)
- BARONIO, Paola  
I-21042 Caronno Pertusella VA (IT)
- BOVISIO, Magda  
I-20151 Milano MI (IT)

(74) Representative: **Adorno, Silvano et al  
Società Italiana Brevetti S.p.A.  
Via Carducci 8  
20123 Milano (IT)**

(56) References cited:  
**GB-A- 1 248 184**

- SHIGA M ET AL: "Characteristic spin fluctuations in  $Y(Mn_{1-x}Al_x)_2$ " JOURNAL OF PHYSICS F. METAL PHYSICS, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 17, no. 8, 1 August 1987 (1987-08-01), pages 1781-1793, XP020043832 ISSN: 0305-4608
- RICHTER ET AL: "The crystallization characteristics of yttrium-aluminum metallic glasses" JOURNAL OF MATERIALS SCIENCE LETTERS, CHAPMAN AND HALL LTD. LONDON, GB, vol. 4, no. 8, 1985, pages 1005-1009, XP009095034 ISSN: 0261-8028
- CH HAUSLEITNER ET AL: "Structural and electronic properties of Y-based metallic glasses" JOURNAL OF PHYSICS: CONDENSED MATTER, INSTITUTE OF PHYSICS PUBLISHING, BRISTOL, GB, vol. 4, no. 48, 30 November 1992 (1992-11-30), pages 9557-9572, XP020056860 ISSN: 0953-8984
- FUKAMICHI ET AL: "Refrigerant characteristics of rare earth-aluminum and rare earth-silicon amorphous alloys" SCIENCE REPORTS OF THE RESEARCH INSTITUTES, TOHOKU UNIVERSITY, SERIES A : PHYSICS, CHEMISTRY AND METALLURGY, TOHOKU UNIV., SENDAI, JP, JP, vol. 36, no. 1, 1991, pages 48-58, XP009095039 ISSN: 0040-8808
- OBI ET AL: "Magnetization and a.c.-susceptibility of amorphous manganese-yttrium and manganese-lanthanum alloys" JOURNAL DE PHYSIQUE. COLLOQUE, PARIS, FR, vol. 49, no. 12 Suppl, December 1988 (1988-12), pages C8-1097, XP009095038 ISSN: 0449-1947

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

- GUO F ET AL: "METALLIC GLASS INGOTS BASED ON YTTRIUM" APPLIED PHYSICS LETTERS, AIP, AMERICAN INSTITUTE OF PHYSICS, MELVILLE, NY, US, vol. 83, no. 13, 29 September 2003 (2003-09-29), pages 2575-2577, XP001046570 ISSN: 0003-6951

## Description

**[0001]** The present invention is directed to non-evaporable getter alloys capable of sorbing different gases but particularly useful for the sorption of hydrogen.

**[0002]** Many applications in the field of industry or research require for their correct working, vacuum or a filling with an atmosphere of a given gas (or gas mixture) in a closed container; examples are the evacuated jackets for thermal insulation (e.g. in thermal bottles, also known as "thermo", or solar collectors), in which in particular the presence of hydrogen is detrimental owing to the high thermal conductivity of this gas; plasma displays; or X-rays generating tubes. The processes for manufacturing these devices comprise a step of container evacuation and possible back-filling thereof with a desired gas; however, these processes always leave traces of undesired gases in the final device. Besides, in the case of hydrogen, whenever a high vacuum or a hydrogen-free gas are produced, mechanisms exist which cause this gas to re-enter the system; these mechanisms are mainly the outgassing of the container walls and the hydrogen permeation across these walls from the external atmosphere toward the container, thus leading to problems in the correct operation of the devices. Owing to the same mechanisms, hydrogen also represents the main contribution to the residual pressure in ultra-high vacuum (UHV) systems, such as the particles accelerators employed in the research field.

**[0003]** To remove traces of unwanted gases from evacuated or gas-filled spaces, it is known to employ non-evaporable getter materials (known in the field as NEG materials, or simply as NEGs), i.e. materials being capable of chemically fixing molecules of gases such as water, oxygen, hydrogen, carbon oxides and, in some cases, nitrogen. In order to accomplish their function, NEGs generally require an initial treatment of thermal activation at temperatures that can vary between about 300 °C up to about 900 °C during a time comprised between few minutes up to several hours, depending on the material composition.

**[0004]** NEGs are generally metals of the III, IV and V transition groups or alloys thereof with other elements, generally other transition metals or aluminum. The most used getter materials are titanium- and, particularly, zirconium-based alloys.

**[0005]** NEG materials show a sorption behavior with respect to hydrogen different from that towards other gases. While for most gases the chemical sorption by these alloys is irreversible, the sorption of hydrogen by NEGs is an equilibrium process reversible as a function of the temperature: hydrogen is efficiently sorbed at relatively low temperatures (under 200-400 °C, according to the chemical composition of the material), but it is released at higher temperatures. The equilibrium features of these materials in sorbing hydrogen are generally represented graphically by means of curves giving, at different temperatures, the equilibrium pressure of hydrogen over the

NEG material as a function of the hydrogen concentration in the same material.

**[0006]** Advantageous features for a NEG material are a low activation temperature and, when hydrogen sorption is considered, a low hydrogen equilibrium pressure in the whole range of temperatures at which the material is to be used.

**[0007]** NEG materials especially suitable for hydrogen sorption are pure yttrium and an alloy disclosed in US pat. No. 3,203,901 and containing, by weight, 84% zirconium and 16% aluminum; both these materials require however relatively high temperatures for their activation, in the range of about 700-900 °C (depending on the degree of activation desired). GB pat. No. 1,248,184 and

15 International patent application publication WO 03/029502 disclose yttrium-rich materials, whose properties are essentially the same as those of pure yttrium; another problem with the materials of GB pat. No. 1,248,184 is that these are essentially mixtures of pure metals, so that at high temperatures they can give rise to evaporation of the metal admixed with yttrium.

**[0008]** Another material widely employed for hydrogen sorption is an alloy of approximate composition, by weight, 80% zirconium, 15% cobalt and 5% mischmetal (a commercial mixture of lanthanum and/or cerium and Rare Earths), disclosed in US pat. No. 5,961,750; this material has the drawback of a relatively high hydrogen equilibrium pressure at temperatures in excess of about 500 °C.

**[0009]** Finally, International patent application publication WO 2006/057020 discloses alloys containing zirconium (as the main component), yttrium and one or more elements chosen among aluminum, iron, chromium, manganese and vanadium for use in hydrogen sorption.

35 The materials of this application have lower activation temperatures compared to the previously mentioned ones; yet, they very poor sorption characteristics for other gases, such as nitrogen.

**[0010]** The thermal expansion and magnetic properties of Y-Mn-Al compositions are reported in the article "Characteristic spin fluctuations in Y(Mn<sub>1-x</sub>Al<sub>x</sub>)<sub>2</sub>" by Shiga et al., published on "Journal of Physics F. Metal Physics", Institute of Physics Publishing, Bristol, GB, Vol 17, no. 8, 1 August 1987, pages 1781-1793.

**[0011]** Object of the present invention is to provide non-evaporable getter alloys that can sorb a wide variety of gasses, and with specially good hydrogen sorption properties.

**[0012]** According to the present invention this object is achieved with non-evaporable getter alloys consisting of by weight, from 60% to 85% yttrium, from 5% to 30% manganese and from 5% to 20% aluminum.

**[0013]** The invention will be described in the following with reference to the drawings wherein:

55

- Figure 1 shows a ternary diagram representing the range of possible compositions of the NEG alloys according to the invention;

- Figures 2a-2d show some possible embodiments of non-evaporable getter devices made by using the alloys of the invention;
- Figures 3 to 6 represent graphs showing the gas sorption features of an alloy of the invention and of some getter materials of the prior art.

**[0014]** The alloys of the invention are those falling within the polygon highlighted in the ternary diagram of weight percentage compositions of Figure 1.

**[0015]** Among these, preferred are the compositions Y 75% - Mn 15% - Al 10% and Y 70% - Mn 18% - Al 12%, represented in Figure 1 as points a and b, respectively.

**[0016]** The alloys of the invention can be prepared by melting in furnace, from pieces or powders of the component metals, taken in the mutual ratios corresponding to the desired final composition. Preferred are the techniques of arc melting under inert gas, e.g. with a pressure of  $3 \times 10^4$  Pascal (Pa) of argon; or in an induction furnace, under vacuum or inert gas. It is however possible to adopt other techniques which are common in the metallurgical field for preparing alloys. Melting requires temperatures higher than 1000 °C.

**[0017]** For the production of getter devices using the alloys of the invention, be these in form of pills of the getter material alone or made with the latter either on a support or in a container, it is preferred to use the alloys in powder form, with particle size generally lower than 250 micrometers ( $\mu\text{m}$ ) and preferably comprised between 40 and 125  $\mu\text{m}$ . Greater particle sizes result in an excessive reduction of the specific surface (surface area per weight unit) of the material, with consequent reduction of the gas sorption properties, in particular the sorption speed at low temperatures; although their use is possible and required in some applications, particles of size less than 40  $\mu\text{m}$  may give rise to problems in the manufacturing steps of getter devices, especially due to their flammability/explosivity when exposed to air.

**[0018]** The shapes in which the getter devices can be prepared by using the alloys of the invention are the most various, comprising pills formed of the getter alloy powders alone, or of these on a metallic support. In both cases the powders can be compacted either by compression or sintering, or both. The pills made only of compressed powders may be used for example in the thermal insulation of thermoses. When the powders are supported, steel, nickel or nickel-based alloys are generally used as supporting material. The support can merely be in form of a strip on the surface of which the alloy powders are caused to adhere by either cold rolling or sintering after deposition by means of various techniques. The support can also be formed as an actual container, having the most various shapes, in which the powders are generally introduced by compression or even without compression in some devices in which the container has the capability to retain powders, either thanks to its shape or because provided with a porous septum permeable to gas flow. Some of these possibilities are illustrated in the

figures 2a-2d: figure 2a shows a pill 20 made of compressed powders only of NEG alloy; Figure 2b shows a NEG device 30 formed of a metallic strip 31 on which powders 32 of NEG alloy are present; figure 2c shows in cross-section a NEG device 40 formed of a metallic container 41 with an upper opening 42 having at the inside thereof powders 43 of NEG alloy; and figure 2d shows in cross-section a NEG device 50 consisting of a metallic container 51 having inside powders 52 of NEG alloy with

5 an upper opening closed by a porous septum 53; a number of other shapes and configurations of devices using the getter alloys of the invention are possible.

**[0019]** The NEG alloys of the invention can be activated by means of treatments of a few tens of minutes at

10 500 °C or at about 300 °C during one or two hours, which are softer conditions than those typically required by pure yttrium or zirconium-aluminum alloys (these latter needing temperatures of about 800-900 °C); furthermore, they show good properties of hydrogen sorption at temperatures lower than those required by using yttrium or compositions of the prior art containing this element as the main component; at the same time, the alloys of the invention show better properties as to sorption of gases different from hydrogen compared to the previously described getter alloys of the prior art (generally containing zirconium as the main component).

**[0020]** The invention will be further illustrated by the following examples. These non-limiting examples describe some embodiments intended to teach those skilled

30 in the art how to put into practice the invention and to represent the best considered mode for carrying out the invention. In the examples, all compositions of the alloys are given as percent by weight of the elements, unless specified otherwise.

## EXAMPLE 1

**[0021]** This example describes the preparation of an alloy of the invention.

**[0022]** An alloy of composition Y 75% - Mn 15% - Al 10%, corresponding to point a in the ternary diagram of figure 1, is produced starting from powders of the component elements weighed in the desired ratio. The powders are mixed and poured into a water cooled copper crucible of an arc furnace under an atmosphere of  $3 \times 10^4$  Pa of argon (so-called "cold-earth" technique). The temperature reached by the mixture during melting is of about 2000 °C, temperature that is maintained during about 5 minutes; the melt is then allowed to cool down to room temperature, obtaining an ingot of the alloy. Since the preparation takes place under conditions of high thermal gradient, in order to enhance the alloy homogeneity the melting is repeated four times. The ingot obtained by cooling after the fourth melting is milled and the resulting powder is finally sieved retrieving the fraction with particle size comprised between 40 and 105  $\mu\text{m}$ .

**[0023]** The thus obtained powder is used to prepare several pills which are used in the gas-sorption tests de-

scribed below: each of the pills, referred to as "sample 1" in the following, are obtained compressing 120 mg of powder under a pressure of 2000 kg/cm<sup>2</sup>.

### EXAMPLE 2

**[0024]** A hydrogen sorption test is carried out on a pill of sample 1 and on a pill of weight 120 mg obtained by compressing powders of pure yttrium. The pills are activated at 500 °C for 30 minutes. The sorption tests are carried out according to the procedure described in the ASTM F 798-82 standard with a test temperature of 400 °C and a hydrogen pressure of  $4 \times 10^{-3}$  Pa: these tests are said to take place under "dynamic conditions" because the test chamber is fed with a variable flow of hydrogen, regulated by means of a feed-back system, in order to have a constant pressure of H<sub>2</sub> over the pill during the test. The results of these tests are graphically represented in Figure 3 as sorption speed, S, measured as cubic centimeters of hydrogen sorbed per second and per gram of alloy (cc/s × g), as a function of the quantity of sorbed hydrogen, Q, measured as cubic centimeters of gas multiplied by the sorption pressure in hectoPascal and normalized per gram of sample (cc × hPa/g); curve 1 corresponds to the pill of sample 1, while the curve corresponding to the pure yttrium sample is labeled Y.

### EXAMPLE 3

**[0025]** In this example are measured the hydrogen equilibrium pressure properties of a sample of an alloy of the invention.

**[0026]** The measurement system is formed as a glass bulb, connected to a pumping apparatus through a liquid nitrogen trap which helps to keep a low background pressure during the test; the sample is heated from the outside of the bulb by radio-frequencies by means of an induction coil. The system is evacuated until a residual pressure of  $1 \times 10^{-4}$  Pa is reached. Under pumping the sample is activated by heating with radio-frequency at 700 °C for an hour. At the end of the activation process the sample is brought to the temperature of 600 °C and the bulb is isolated from the pumping apparatus. A measured quantity of hydrogen is introduced into the bulb and the pressure variations are measured by means of a capacitance manometer; the pressure value at which the system stabilizes provides the equilibrium pressure under those conditions. Such a procedure is repeated several times, introducing each time a different quantity of hydrogen into the system. From the measurement of the equilibrium pressures, being known the system volume and the weight of the sample, the concentration of hydrogen sorbed by the sample under the different measurement conditions is obtained.

**[0027]** With the measurement system and procedure above described, the values of equilibrium pressure of hydrogen over a pill of sample 1 are measured; these values are graphically represented as curve 1 in figure

4, showing the equilibrium pressure, P, measured in hectoPascal (hPa), as a function of the sorbed hydrogen concentration, C, measured in cubic centimeters of gas multiplied by the sorption pressure and normalized per milligram of alloy (cc × hPa/mg). For comparison, in the same graph are also shown two segments representing the hydrogen equilibrium properties of two prior art materials, considered in the field as particularly suitable for the sorption of hydrogen; in particular, segment 2 represents the properties of an alloy of composition Zr 84% - Al 16% (whose features and preparation are described in US patent No. 3,203,901), while segment 3 represents the properties of an alloy of composition Zr 80.8% - Co 14.2% - mischmetal 5.0% (known from US patent No. 5,961,750). Segments 2 and 3 are portions of lines obtained by averaging the data resulting from a number of experimental tests carried out in the past with said known alloys in the same conditions as described above for sample 1.

### EXAMPLE 4

**[0028]** The tests of example 3 is repeated, measuring in this case the hydrogen equilibrium pressure at 700 °C of pills corresponding to sample 1 and to the same Zr-Al and Zr-Co-mischmetal alloys. The results of these tests are graphically represented in figure 5, again with curve 1 representing the properties of sample 1 and segments 2 and 3 representing the properties of the Zr-Al alloy and of the Zr-Co-mischmetal alloy, respectively.

### EXAMPLE 5

**[0029]** A series of carbon monoxide (CO) sorption tests is carried out on a pill of sample 1 and on pills of the same Zr-Al and Zr-Co-mischmetal alloys of example 3; these pills of prior art alloys have the same weight of the pill of sample 1. These tests are carried out under "dynamic conditions", according to the standard ASTM F 798-82, as described in example 2. The pills are activated at 500 °C for 10 minutes, and the tests are carried out at 400 °C, with a constant CO pressure of  $4 \times 10^{-3}$  Pa. The results of these tests are reported graphically in figure 6, as CO sorption speed (measured in cubic centimeters of CO per second, cc/s) as a function of the quantity of CO sorbed (measured in cubic centimeters of sorbed CO multiplied by the test pressure, cc × hPa).

### Discussion of the results

**[0030]** The graph of figure 3 confirms that the alloys of the invention have better hydrogen sorption properties than those of a sample of pure yttrium activated under the same conditions.

**[0031]** The graphs of figures 4 and 5 show that the alloys of the invention have better hydrogen equilibrium properties compared to two alloys of the prior art that are considered in the field as having particularly good fea-

tures as regards this parameter.

[0032] Finally, figure 6 shows that the alloys of the invention also have better sorption properties for an oxygenated gas (CO) compared to the same two prior art alloys employed for the comparison of examples 3 and 4.

## Claims

1. Non-evaporable getter alloys consisting of, by weight, from 60% to 85% yttrium, from 5% to 30% manganese and from 5% to 20% aluminum. 10
2. Alloy according to claim 1 of weight composition Y 75% - Mn 15% - Al 10% 15
3. Alloy according to claim 1 of weight composition Y 70% - Mn 18% - Al 12%. 20
4. Non-evaporable getter device comprising an alloy of claim 1 in form of powders with particle size of less than 250  $\mu\text{m}$ . 25
5. A device according to claim 4, wherein said powders have particle size comprised between 40 and 125  $\mu\text{m}$ . 30
6. A device (20) according to claim 4, consisting of a pill of compressed powders only of the getter alloy. 35
7. A device (30) according to claim 4 formed of a metallic strip (31) on which powders (32) of the getter alloy are present, which are caused to adhere to said strip by cold rolling or deposition followed by sintering. 40
8. A device (40) according to claim 4, consisting of a container (41) with an upper opening (42) and powders (43) of the getter alloy, which are inside this container (41). 45
9. A device (50) according to claim 4, consisting of a container (51) and powders (52) of the getter alloy which are inside this container (41); this container having an upper opening closed by a porous septum (53). 50

## Patentansprüche

1. Nicht-evaporierbare Getterlegierungen, bestehend aus von 60% bis 85% Yttrium, von 5% bis 30% Mangan und von 5% bis 20% Aluminium, jeweils bezogen auf Gewichtsprozent.
2. Legierung nach Anspruch 1 mit der Gewichtszusammensetzung Y 75% - Mn 15% - Al 10%. 55

3. Legierung nach Anspruch 1 mit der Gewichtszusammensetzung Y 70% - Mn 18% - Al 12%. 5
4. Nicht-evaporierbare Gettervorrichtung umfassend eine Legierung nach Anspruch 1 in Form von Pulvern mit einer Partikelgröße von weniger als 250  $\mu\text{m}$ . 10
5. Eine Vorrichtung nach Anspruch 4, worin die Pulver eine Partikelgröße im Bereich zwischen 40 und 125  $\mu\text{m}$  aufweisen. 15
6. Eine Vorrichtung (20) nach Anspruch 4, bestehend aus einer Tablette aus komprimierten Pulvern ausschließlich der Getterlegierung. 20
7. Eine Vorrichtung (30) nach Anspruch 4, gebildet aus einem metallischen Band (31) auf dem Pulver (32) der Getterlegierung vorliegen, welche durch Kaltwalzen oder Abscheiden gefolgt von Sintern auf dem Streifen befestigt wurden. 25
8. Eine Vorrichtung (40) nach Anspruch 4, bestehend aus einem Behälter (41) mit einer oberen Öffnung (42) und Pulvern (43) der Getterlegierung, welche sich innerhalb dieses Behälters (41) befinden. 30
9. Eine Vorrichtung (50) nach Anspruch 4, bestehend aus einem Behälter (51) und Pulvern (52) der Getterlegierung, welche sich innerhalb dieses Behälters (41) befinden; wobei dieser Behälter eine obere Öffnung aufweist, die durch ein poröses Septum (53) verschlossen ist. 35

## Revendications

1. Alliages getter non évaporables composés, en poids, de 60 % à 85 % d'yttrium, de 5 % à 30 % de manganèse et de 5 % à 20 % d'aluminium. 40
2. Alliage selon la revendication 1, d'une composition en poids de Y 75 % - Mn 15 % - Al 10 %. 45
3. Alliage selon la revendication 1, d'une composition en poids de Y 70 % - Mn 18 % - Al 12 %. 50
4. Dispositif getter non évaporable comprenant un alliage selon la revendication 1 sous la forme de pou- dres de taille de particule inférieure à 250  $\mu\text{m}$ . 55
5. Dispositif selon la revendication 4, dans lequel les- dites poudres ont une taille de particule comprise dans la plage allant de 40 à 125  $\mu\text{m}$ . 60
6. Dispositif (20) selon la revendication 4, constitué d'une pastille de poudres comprimées constituée uniquement d'alliage getter. 65

7. Dispositif (30) selon la revendication 4, formé d'une bande métallique (31) sur laquelle les poudres (32) de l'alliage getter sont présentes que l'on pousse à adhérer à ladite bande par laminage ou dépôt à froid suivie par un frittage. 5

8. Dispositif (40) selon la revendication 4, constitué d'un conteneur (41) ayant une ouverture supérieure (42) et de poudres (43) de l'alliage getter qui sont à l'intérieur du contenant (41). 10

9. Dispositif (50) selon la revendication 4, constitué d'un conteneur (51) et de poudres (52) de l'alliage getter qui sont à l'intérieur du conteneur (51), ce conteneur ayant une ouverture supérieure fermée par un septum poreux (53). 15

20

25

30

35

40

45

50

55

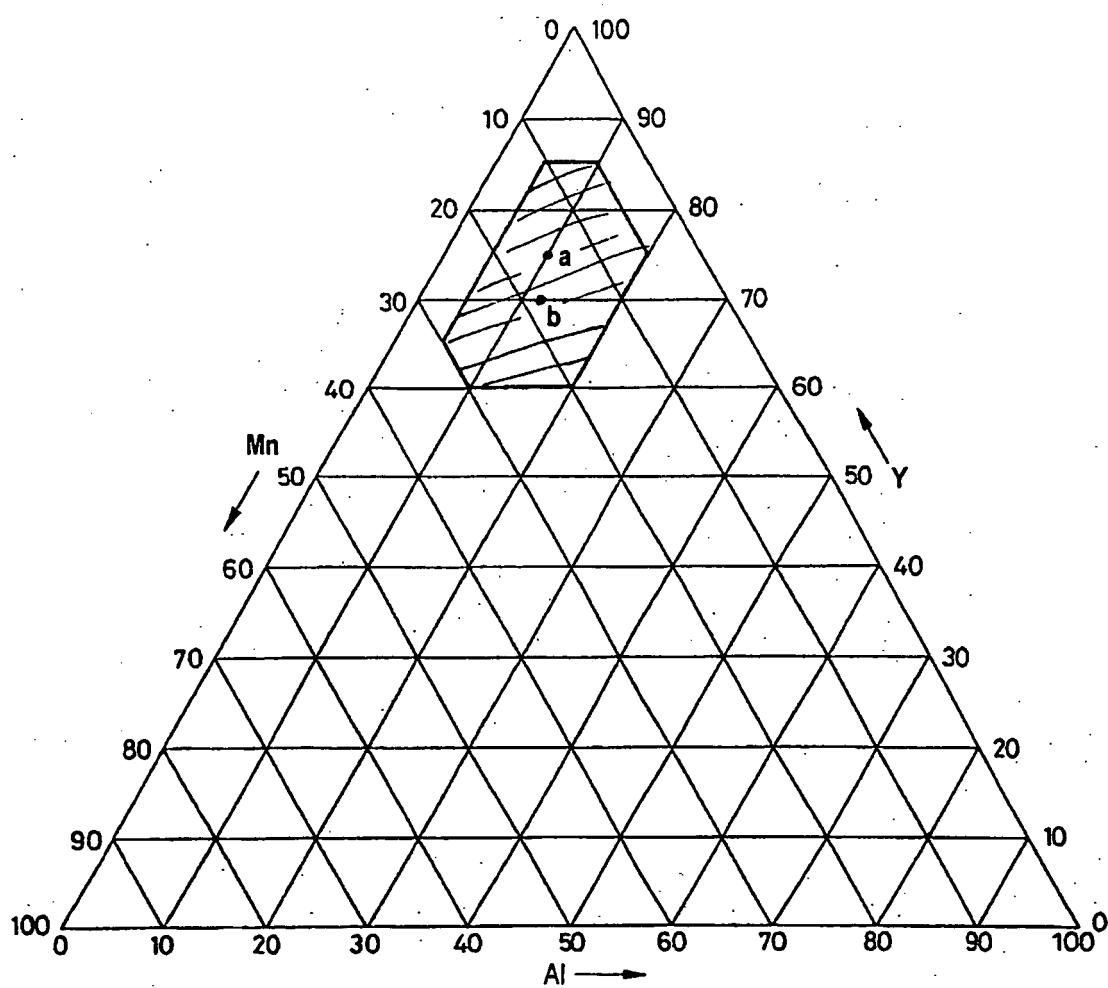


Fig. 1

Fig. 2a

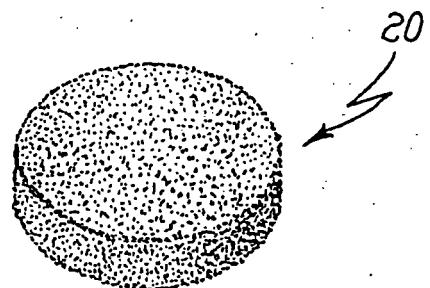


Fig. 2b

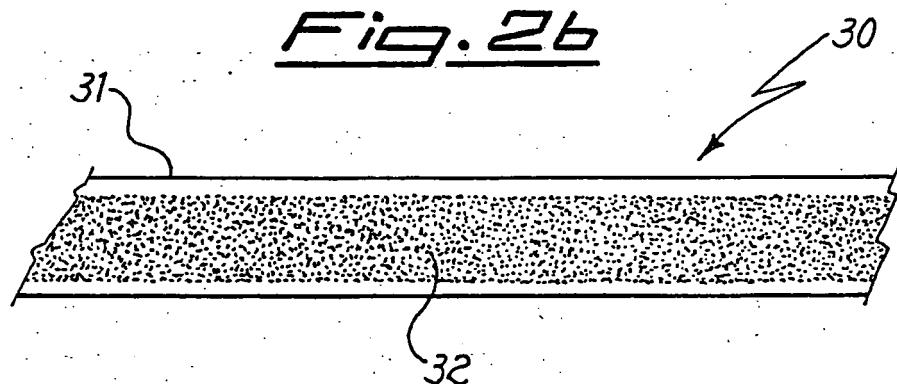


Fig. 2c

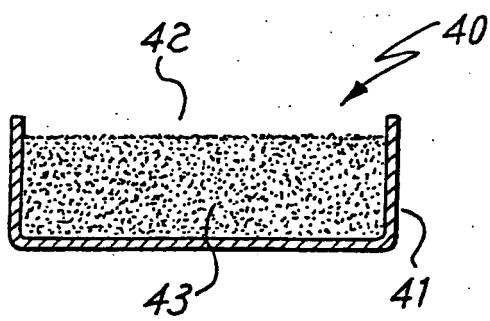
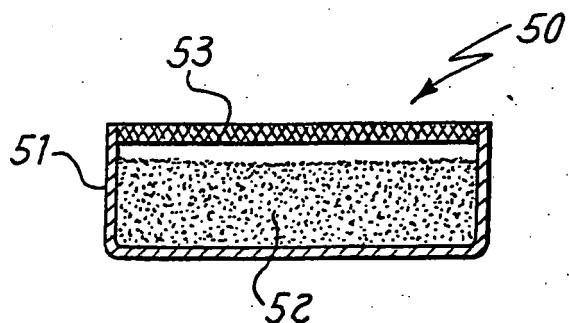


Fig. 2d



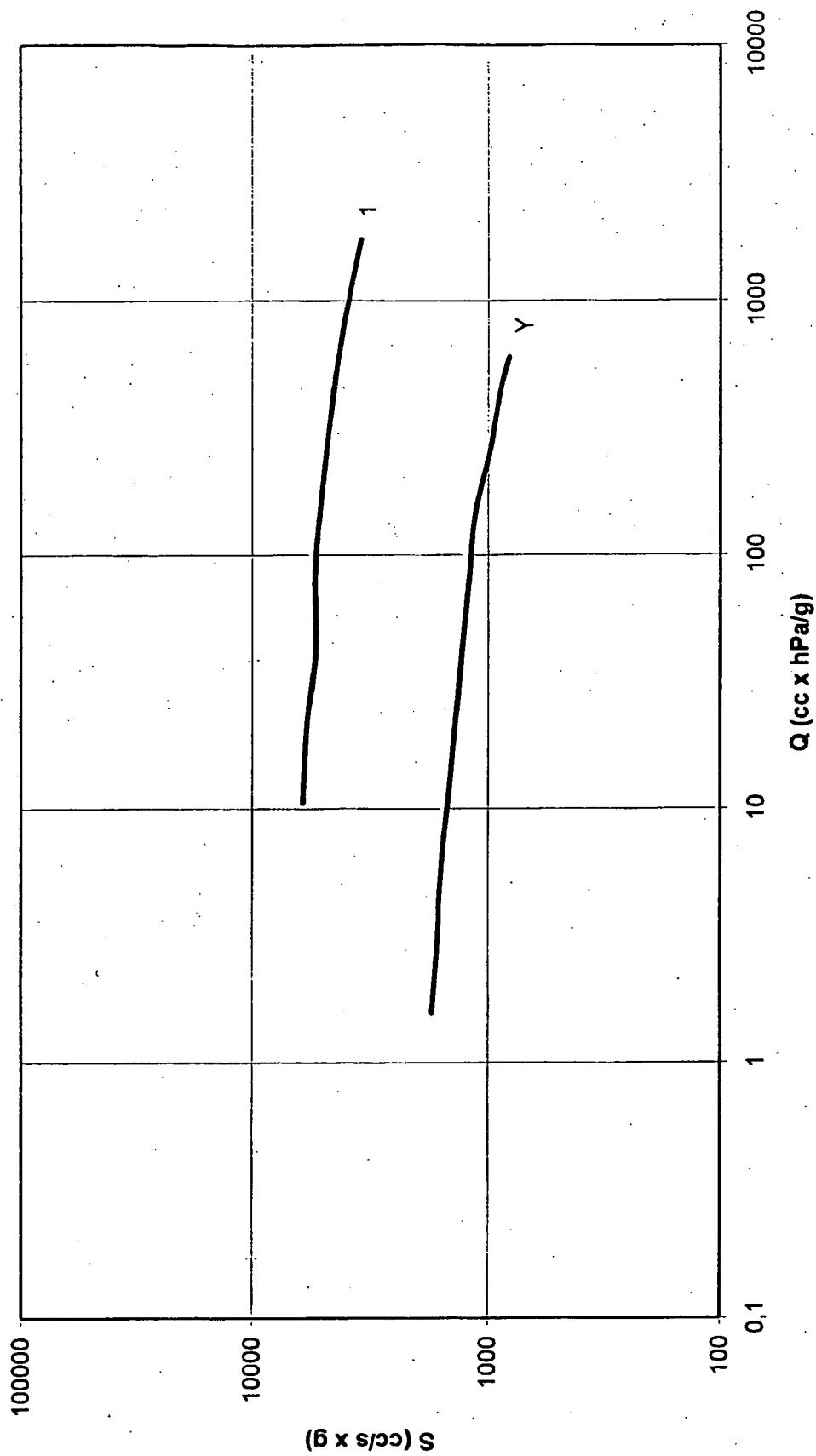
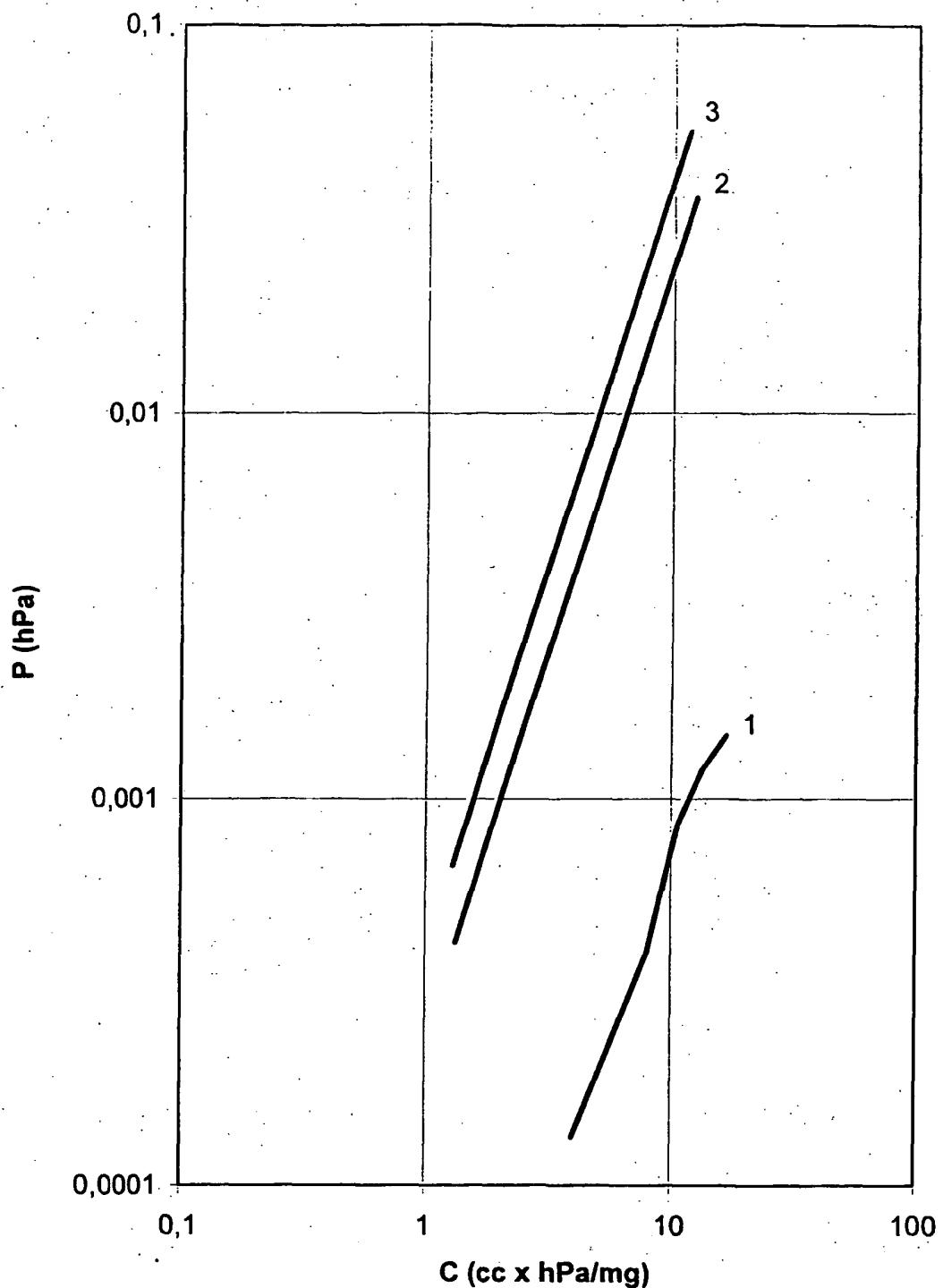
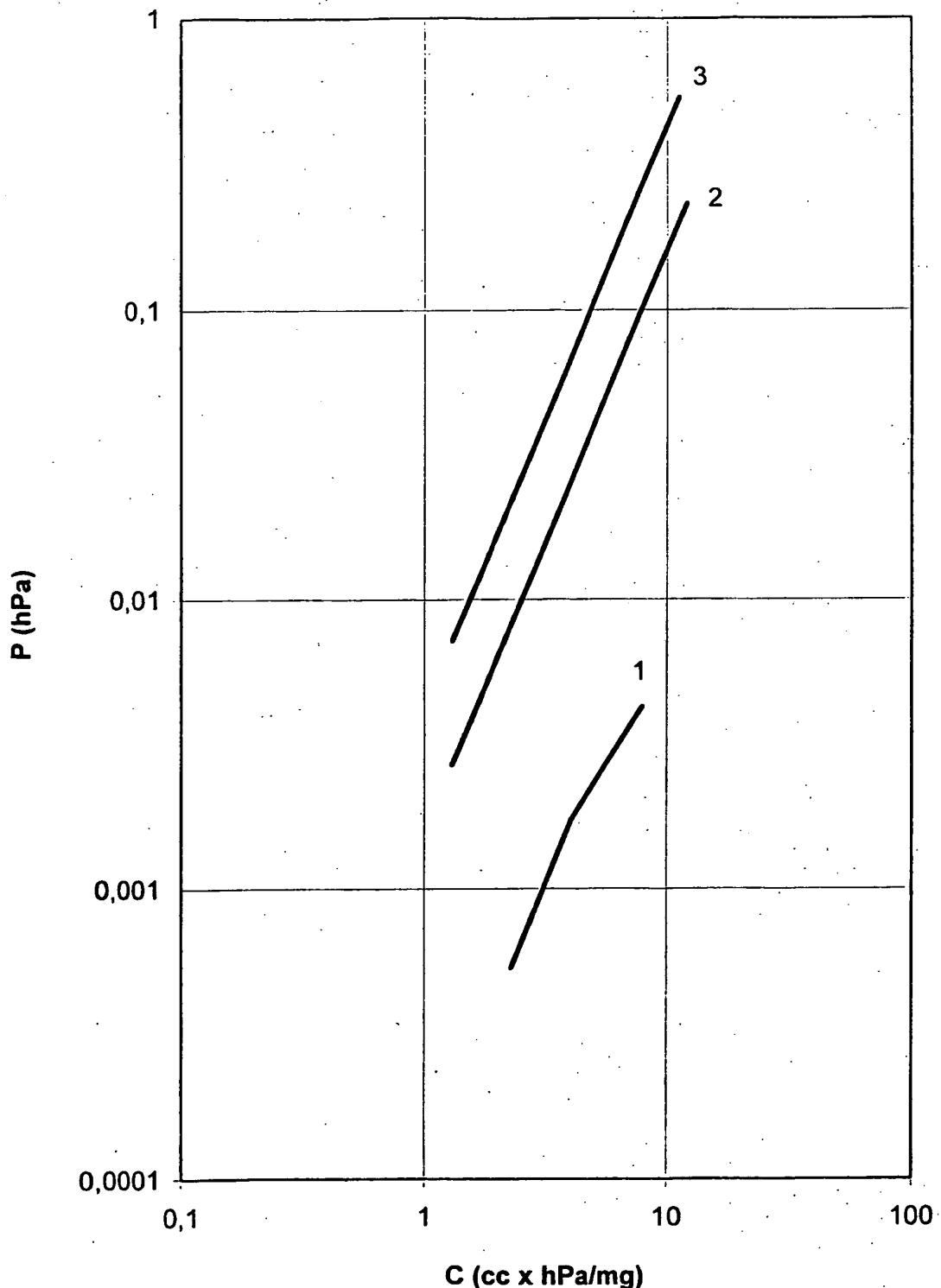


Fig. 3



**Fig. 4**



**Fig. 5**

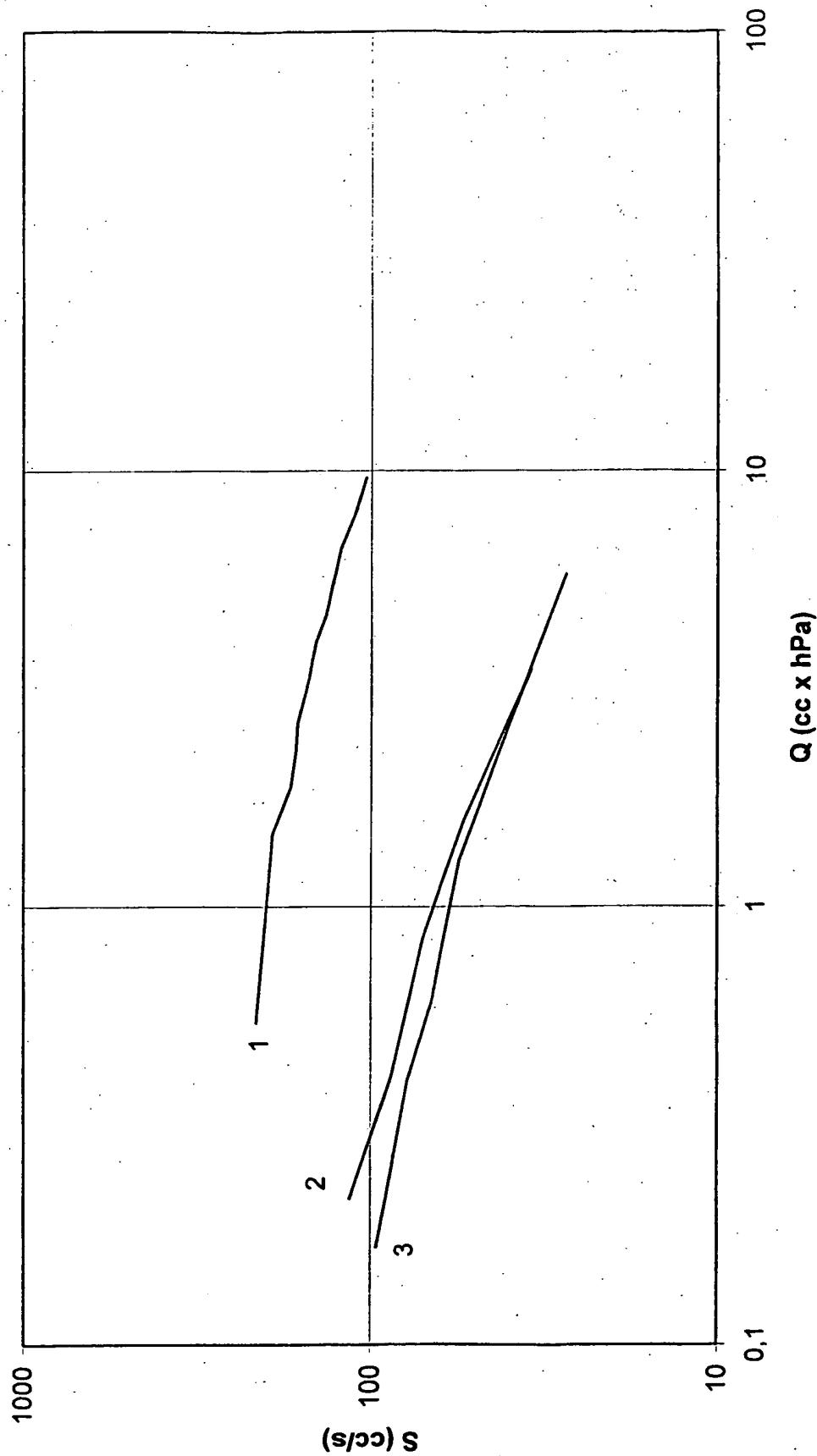


Fig. 6

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- US 3203901 A [0007] [0027]
- GB 1248184 A [0007]
- WO 03029502 A [0007]
- US 5961750 A [0008] [0027]
- WO 2006057020 A [0009]

**Non-patent literature cited in the description**

- Characteristic spin fluctuations in  $Y(Mn_{1-x}Al_x)$ . **Shiga et al.** Journal of Physics F. Metal Physics. Institute of Physics Publishing, Bristol, 01 August 1987, vol. 17, 1781-1793 [0010]